

# Wide Band Gap CuInSe<sub>2</sub> and CdTe-based Thin Films for Tandem Solar Cells

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## ABSTRACT

Cd<sub>1-x</sub>Zn<sub>x</sub>Te and CuIn<sub>1-x</sub>Ga<sub>x</sub>(Se<sub>1-y</sub>S<sub>y</sub>)<sub>2</sub> (CIGSS) are being investigated as absorber layer materials for the wide band gap cell in a tandem or multijunction thin film solar cell. In each case, the composition can be changed to continuously vary the band gap over a wide range, including the range  $1.7 \leq E_g \leq 1.9$  eV which will be required in an optimized tandem configuration. Cd<sub>1-x</sub>Zn<sub>x</sub>Te alloy films with x from 0 to 1 and band gap from 1.5 to 2.25 eV have been deposited by co-evaporation from binary CdTe and ZnTe sources. Control of the Cd<sub>1-x</sub>Zn<sub>x</sub>Te alloy film composition, band gap, and lattice constant are demonstrated. A five source evaporation system for the deposition of CIGSS films has been designed and constructed with special concern given to control of the chalcogen sources.

## Introduction

To become a viable option for high performance photovoltaics, tandem or multijunction solar cells based on polycrystalline thin films will require a wide band gap top cell with at least 15% efficiency, optical band gap in the range  $1.7 \leq E_g \leq 1.9$  eV, and small sub-band gap absorption. The wide band gap cell must be identified and developed before other critical issues can be fully addressed since the rest of the tandem device structure and processing will be determined largely by the choice of wide band gap cell.

In this program, IEC is investigating options for the wide band gap cell based on Cd<sub>1-x</sub>Zn<sub>x</sub>Te and CIGSS alloys. The pseudobinary system based on CdTe and ZnTe allows formation of Cd<sub>1-x</sub>Zn<sub>x</sub>Te alloys with a continuous band gap range from 1.5 eV to 2.25 eV, with the alloy range  $0.35 < x < 0.6$  giving the desired band gap range. With CIGSS films the band gap can be continuously varied by changing either the relative Ga/In or S/Se compositions. However, sufficient alloying with either one alone to give band gap greater than about 1.3 eV decreases device performance. In the pentenary material CIGSS, the cation and anion alloying concentrations can be kept to a minimum. Admittance spectroscopy has suggested that the pentenary alloys have lower defect concentrations than CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> or CuIn(Se<sub>1-y</sub>S<sub>y</sub>)<sub>2</sub> films with comparable band gap [1].

## Cd<sub>1-x</sub>Zn<sub>x</sub>Te Deposition

The deposition of thin Cd<sub>1-x</sub>Zn<sub>x</sub>Te films with controlled compositions is facilitated by the congruent sublimation of CdTe and ZnTe compounds so that single-phase alloy films can be deposited by evaporation from binary compound CdTe and ZnTe sources. Radiatively

heated boron nitride effusion cells were used to sublime coarse, 6N pure CdTe and ZnTe powders at a source to substrate distance of 20 cm. Sublimation of the compounds proceeds via:  $\text{CdTe} \rightarrow \text{Cd} + \frac{1}{2}\text{Te}_2$  and  $\text{ZnTe} \rightarrow \text{Zn} + \frac{1}{2}\text{Te}_2$ . The alloy composition of the film is determined by the ratio of elemental impingement rates and their relative sticking coefficients. The impingement rates are determined by the effusion rates from the CdTe and ZnTe sources and are controlled by source temperature.

To deposit alloy films at a reasonable growth rate, ~0.3  $\mu\text{m}/\text{min}$ , a CdTe source temperature of 900°C was selected and alloy compositions were varied by adjusting the ZnTe source temperature. Composition was determined by energy dispersive x-ray spectroscopy (EDS) and lattice parameter determination from x-ray diffraction (XRD) measurements, using the Nelson-Riley-Sinclair-Taylor analysis. Cd<sub>1-x</sub>Zn<sub>x</sub>Te films 3-4  $\mu\text{m}$  thick with x from 0 to 1 were deposited onto ITO/glass and CdS/ITO/glass substrates at 325°C. The film compositions agree well with the effusion rate composition showing that, for the chosen substrate temperature of 325°C, the Cd and Zn sticking coefficients are comparable and, therefore, likely very high. The optical band gap was determined from an extrapolation of  $\alpha^2$  versus energy, where  $\alpha$  is the absorption coefficient obtained from transmission and reflection data. Results on CdS/ITO/7059 glass substrates are summarized in Table 1 and the band gap and lattice parameter are plotted as a function of x in Figure 1. Atomic force and scanning electron microscopy showed the presence of faceted grains with decreasing lateral dimension as relative ZnTe content increases. X-ray diffraction patterns indicated the presence of a single crystalline phase in all cases. All films exhibited sharp reflections and strong (111) texture, indicative of homogeneous composition.

Table 1. Composition and band gap of Cd<sub>1-x</sub>Zn<sub>x</sub>Te films. The effusion rate ratio is defined as  $r_{\text{eff}} = r(\text{ZnTe})/[r(\text{ZnTe}) + r(\text{CdTe})]$ .

$r_{\text{eff}}$	x(EDS)	x(XRD)	$E_g$ (eV)
0.02	0	0.06	1.52
0.10	0.15	0.10	1.56
0.30	0.31	0.31	1.67
0.31	0.33	0.30	1.69
0.43	0.40	0.37	1.75
0.46	0.42	0.46	1.77
0.92	0.93	0.92	2.19
1.00	1.0	1	2.24

Efforts are underway to characterize the control of film properties during post-deposition treatments. This will include halide and air treatments of Cd<sub>1-x</sub>Zn<sub>x</sub>Te alloy

films, which are typically used to optimize CdTe cell performance. In addition, solar cells are being fabricated and characterized.

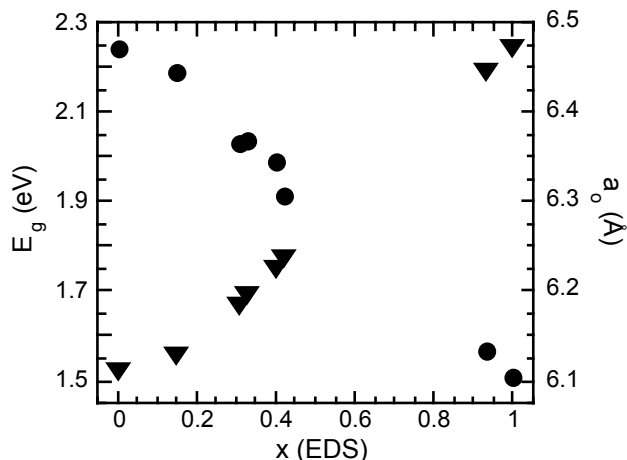


Fig. 1. Variation in band gap ( $\tau$ ) and lattice parameter ( $\lambda$ ) with x for  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  films.

### $\text{CuIn}_{1-x}\text{Ga}_x(\text{Se}_{1-y}\text{S}_y)_2$ Deposition

A new system has been constructed to deposit CIGSS films by five source elemental thermal evaporation. Sequential processes, in which metal or binary layers are deposited at low temperature and then reacted in mixed hydride gases or elemental vapors, were ruled out due to difficulties in attaining uniform incorporation of Ga and In.

An illustration showing the layout of the deposition system and a side view photograph are shown in Figures 2 and 3, respectively. Boron nitride crucibles are used as sources for Cu, In, and Ga. These crucibles are heated in a boron nitride furnace, using tantalum wire resistive heaters, and multiple layers of thermal shielding. While these metal sources typically operate at temperatures

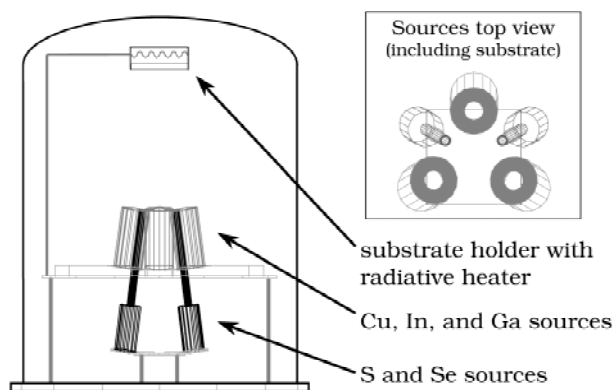


Fig. 2. Illustration of the layout for the 5 source CIGSS evaporation system.

between 1100°C and 1400°C, the evaporation temperatures for Se and S will range from 100 to 300°C. The chalcogen sources are mounted below the metal sources to increase the distance, minimizing thermal cross talk, and a new source design was developed to facilitate precise thermal control. The crucible for the S and Se sources consists of a stainless steel bottle connected to a tube that enables the S or Se vapor to pass between two of the metal sources. The S and Se sources have a tapered shape to fit snugly in the stainless steel heater, which is heated by an electrically insulated tantalum wire. A water-cooled jacket surrounds each source to decrease the thermal response time and enhance control at low temperatures. The nozzles from all five sources are at the same height, 25 cm from the substrate. The entire setup is mounted on a base plate in a bell jar system using a water cooled stainless steel bell jar with base pressure  $\sim 1 \times 10^{-6}$  T. All components of the system are designed to withstand the corrosivity of the S vapor and the chamber includes a chilled Meissner trap to getter excess sulfur.

Calibration of the sources is underway so that processes to deposit CIGSS films with uniform, controlled composition can be developed.

### Acknowledgement

This work is supported by NREL subcontract AAT-1-30620-07 under the High Performance Photovoltaics Initiative.

### Reference

- [1] Friedlmeier, T.M. and H.W. Schock, Proc. 2<sup>nd</sup> World Conf. on Photovoltaic Solar Energy Conversion, Vienna, European Commission, (1997) 1117.

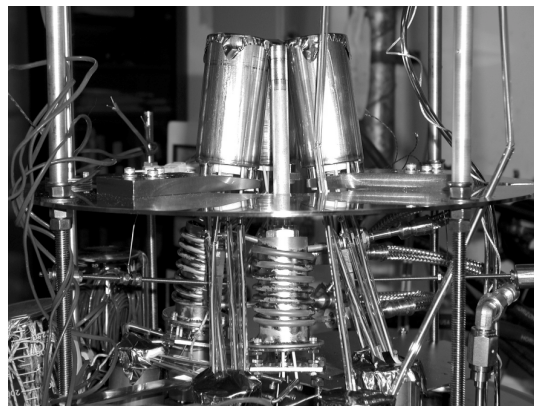


Fig. 3. Side view of the source setup showing S and Se sources mounted below the metal sources.